DMIC review OF RECENT DEVELOPMENTS

Oxidation-Resistant Coatings for Refractory Metals

B. C. Allen • November 17, 1971

On September 21-22, 1971, an information exchange on coated refractory metals was held at the NASA Lewis Research Center in Cleveland, Ohio. Among other benefits, this forum served to identify most of the current research and development activity on coated refractory metals. As a reader service, MCIC has identified these programs in Table 1 along with a listing of the sponsoring agencies and participating organizations and personnel. About two weeks later, several of these same contractors presented formal summaries of their experimental work at a National SAMPE meeting on Space Shuttle materials in Huntsville, Alabama. Highlights from some of these presentations follow.

EVALUATION OF COATED COLUMBIUM AND TANTALUM ALLOYS FOR SPACE SHUTTLE APPLICATIONS

An evaluation of fused slurry silicide coated columbium alloys for use in reentry heat shields is under way at General Dynamics.[1] At present, flight simulation specimens have been subjected to simulated 1-hour reentry cycles involving temperatures to 2400 F. Of 36 Sylvania Si-20Cr-20Fe (R512E) coated Cb-752 and C-129Y columbium alloy specimens, 35 survived 100 cycles. Of 20 Vac-Hyd Si-Hf-Ta-Cr-Fe (VH-109) coated Cb-752 and C-129Y columbium alloy specimens, 19 failed structurally in 42 to 96 cycles, and one specimen survived 100 cyclic exposures. For all specimens that survived 100 cycles, room-temperature tensile strength based on uncoated cross sectional area was reduced 10 to 15 percent, while the elongation in 2 inches was roughly one-third the nominal 10 to 15 percent for unexposed specimens. Steady-state creep tests of R512E/C-129Y specimens have been made. Specimens for lightning-strike and micrometeroid tests are being prepared. Subsize open corrugation panels and a rib stiffened thermal protection system (TPS) are being designed and fabricated. Some details concerning the preparation of the Vac-Hyd coating used have been released.[2]

As indicated above, failure refers to the inability of the coated system to support a load. Until recently, a coating system was considered to have failed at the first signs of substrate oxidation. However, on the basis of work performed over about the past 5 years on the ASSET and ASCEP programs and on programs at Pratt and Whitney and McDonnell Douglas Astronautics regarding structural testing of coated columbium alloys, considerable tolerance for coating defects has been found. Therefore, a failure criterion based on structural integrity appears to be more realistic and useful for design purposes than one based on visual inspection.

Progress toward the evaluation and re-use capabilities of coated columbium alloys for TPS has been described at Battelle-Columbus.[3,4] The effect of intentional coating defects has been investigated on the coating systems, R512E/Cb-752, R512E/FS-85, and VH-109/C-129Y. Dynamic tests have been conducted on sheet specimens in air using a 1.5 MW plasma arc facility which simulated reentry conditions of temperature, pressure (12 torr), velocity (mach 4.5), free-stream enthalpy (6700 Btu/lb), heat flux (28-38 Btu/ft^2 sec), and aerodynamic shear (2.0 to 2.6 lb/ft^2) under wedge type flow conditions.[5] Defects in all three systems grew at a low rate of 0.01 to 0.1 mil/minute below 2470 F and 10 to 20 mils/minute at higher temperatures. Although there was evidence of molten oxide formation, catastrophic auto-ignition effects were not observed at temperatures to 2600 F.

Below 2470 F, property degredation was controlled primarily by substrate contamination from oxygen admitted at defect sites. Coating cracks were simulated by intentional defects 4 mils in diameter extending 1 to 2 mils into the substrate. The kinetics of contamination were slower than parabolic and suggested a self-healing mechanism was operative. Such behavior was not apparent in the case of 40-mil defects which led to more rapid contamination by the expected parabolic kinetics. Tensile tests have been conducted on specimens having a gage width 30 times the coating defect width and 5 to 10 times the substrate contamination spot width.[4] After 1 plasma cycle, there was no loss in room-temperature tensile properties. After 5 cycles, fracture originated at the contamination spot, but failure was predominately ductile with no loss of substrate strength. By a small margin, C-129Y columbium alloy gave the lowest contamination rate and decrease in ductility.

The variation of R512E and VH-109 coating thickness on Cb-752 and C-129Y columbium alloy substrates has been studied.[6] Thickness was determined on metallographic sections and correlated with other methods including micrometer, eddy current, and thermoelectric probe. Generally, the best correlation was achieved with pointed-anvil micrometer measurements. At the nominal 3-mil level, the R512E coating was more uniform since the intralot thickness variation at the 99 percent confidence level was 0.070 mils compared with ± 1.07 mils for VH-109.

Practical field repair of fused slurry silicide coated columbium alloys has been demonstrated.[7] A hand-held portable infrared heater using argon gave effective repairs by heating small areas of R512E repair coated Cb-752 columbium alloy for

TABLE 1. TOPICS DISCUSSED IN SEPTEMBER 1971 MEETING AT NASA LEWIS RESEARCH CENTER

Investigators	Affiliation	Contract Number	Topic
S. R. Levine S. J. Gerardi R. A. Perkins R. V. Warnock	NASA-Lewis Vac-Hyd Lockheed Space and Missiles Solar Division International Harvester	- NAS 8-27280 NAS 3-14316 NAS 3-14315	Development of coatings for columbium and tantalum alloys
B. G. Fitzgerald	McDonnell Douglas	NAS 3-15546	Contamination tolerance coated columbium alloys
J. D. Culp	Astronautics East	NAS 8-26121	Coating field-repair methods[7,8]
B. D. Reznik	Sylvania	NAS 3-14307	Merits of oxidation-resistant layer between coating and substrate
E. S. Bartlett	Battelle Columbus	NAS 8-26205 NAS 8-26225	Contamination, coating defect growth, and properties of coated columbium alloys exposed to high mass flow conditions[3,4]
W. E. Black	General Dynamics/ Convair	NAS 1-9793	Preparation and elevation of coated columbium alloy heat shields[1]
R. H. Witt	Grumman Aerospace	-	Preparation and evaluation of R512C/Ta-10W elevon
N. M. Geyer	AFML	F33615-69-C-1634	Preparation and evaluation of R512E/FS-85 burner cans
F. J. Centolanzi W. P. Gilbraeth	NASA-Ames	-	Arc jet studies on the effect of dissociated oxygen on superalloys and coated columbium alloys

2 minutes at 2700 F. The oxidation performance was equivalent to that of the virgin coating. Torch heating also was used with good results.[8]

Manlabs has reported part of its work on an extensive Air Force-sponsored program of evaluating the stability characteristics of refractory materials under reentry and high-velocity atmospheric flight conditions.[9] Among the many systems studied were two coated refractory metals, R512E/Cb-752 and R512C (Si-20Ti-10Mo)/T-222. Oxidation tests in flowing air were conducted in (1) furnace, (2) high-velocity subsonic flow using induction heating --performed at Lockheed Palo Alto Research Laboratory, and (3) plasma arc normal to the surface --performed in the Avco-SSD Model 500 and ROVERS facilities.[10] Test conditions are summarized in Table 2 and indicate that failure depended primarily on surface temperature and not on air flow rate or pressure in the ranges investigated. R512E/Cb-752 and R512C/T-222 survived to temperatures of about 2900 and 3100 F, respectively, at 0.5 hours. However, on the basis of sections taken on failed plasma-arc specimens, surface-recession rates appeared low at 0.01 atmosphere. At 1 atmosphere, surface-recession rates appeared to be very great and suggest catastrophic oxidation. The spectral normal emittance at 0.65 micron appeared to be stable in the 0.8 to 0.9 range during the high-velocity tests. In the plasma-arc tests the total normal emittance averaged 0.56 or 0.57 and served as an indicator for change in resistance and signalled coating failure.

OXIDATION OF COATED UNALLOYED COLUMBIUM

The oxidation behavior of $MoSi_2$ coated columbium has been studied in West Germany.[11] The oxidation kinetics of $MoSi_2$ were compared with $CbSi_2$. Compared with $CbSi_2$, $MoSi_2$ was shown to exhibit a broader range of temperature and oxygen partial pressures in which a protective layer of SiO_2 formed. Furthermore the diffusion of silicon from $MoSi_2$ into the substrate through a $(Mo+Cb)_5Si_3$ layer was slower by a factor of 3 to 4 than similar diffusion through a Mo_5Si_3 layer. Thus, columbium dissolved in Mo_5Si_3 was an effective barrier against inward diffusion of silicon from $MoSi_2$. Also, the thermal expansion coefficients of $MoSi_2$ and $(Mo+Cb)_5Si_3$ were similar to that of the substrate. Test samples were prepared by powder metallurgy by depositing $MoSi_2$ on columbium and hot pressing. The coating was protective for one 1000-hour cycle in air at 2640 F. On cooling, the SiO_2-rich layer tended to spall. Although the cracks healed on reheating, reformation of the protective layer caused increased consumption of silicon from the coating.

United Aircraft has compared the oxidation behavior of columbium coated with (1) R512E, (2) pack $CbSi_2$, and (3) equal thickness layers of Cb_5Si_3 and $CbSi_2$ applied by an unspecified process.[12] Coating (3) appeared to be the most oxidation resistant after 20 hours in static air, as indicated in Figure 1. In cyclic tests after twenty-four 1-hour cycles to 1830 F, oxide-filled cracks and substrate oxidation were observed for R512E and $CbSi_2$ coated specimens. The $Cb_5Si_3/CbSi_2$ coating remained crack free and protective.

TUNGSTEN-SILICON-OXYGEN INTERACTIONS

The interaction of silicon and oxygen with an electrically heated tungsten ribbon has been studied.[13] The kinetics and mechanism of low-pressure (under 1×10^{-3} torr) oxidation of tungsten silicides to 2550 F have been determined. Activation energies for oxygen consumption were presented.

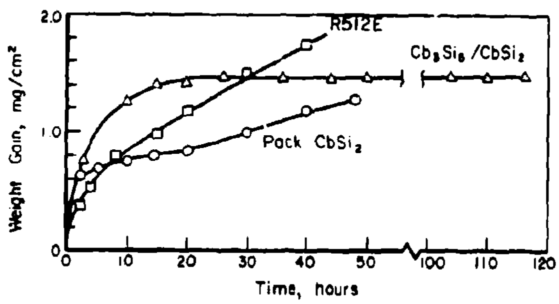

FIGURE 1. STATIC OXIDATION BEHAVIOR OF SILICIDE COATED COLUMBIUM AT 1830 F IN AIR[12]

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(3) Bartlett, E. S., and Maykuth, D. J., "Coated Columbium Flaw Growth in the Space Shuttle Environment", Columbus Laboratories, Battelle Memorial Institute, Columbus, O., paper presented at National SAMPE Technical Conference, October 5-7, 1971, Huntsville, Ala.

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(5) Grinberg, I. M., Luce, R. G., and Stephan, J. G., "Plasma Arc Testing Techniques for Space Shuttle TPS Materials", Columbus Laboratories, Battelle Memorial Institute, Columbus, O., paper presented at National SAMPE Technical Conference, October 5-7, 1971, Huntsville, Ala.

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TABLE 2. CONDITIONS CAUSING FAILURE OF COATED COLUMBIUM AND TANTALUM ALLOYS[10]

Environment	Air Pressure, atm	Velocity	Exposure Time, hr	Stagnation Enthalpy Btu/lb	Heat Flux, Btu/Ft² sec	Maximum Surface Temperature, F
			R512E/Cb-752			
Furnace cold gas/hot wall	1	1.8 ft/sec	1	-	-	2750
High Velocity cold gas/hot wall	1	50 ft/sec	0.5	-	-	~2900
Plasma Arc hot gas/cold wall	1	mach 0.1-0.2	0.5	5,500	275	2940
	0.01	mach 3.2	0.5	13,000	225	2940
			R512C/T-222			
Furnace cold gas/hot wall	1	1.8 ft/sec	1	-	-	3250
High Velocity cold gas/hot wall	1	10 ft/sec	0.5	-	-	~3000
Plasma Arc hot gas/cold wall	1	mach 0.1-0.2	0.5	5,500	275	3100
	0.01	mach 3.2	0.5	13,000	225	3100

(7) Reznik, B. D., "Practical Field Repair of Fused Slurry Silicide Coating for Space Shuttle T.P.S", Sylvania Electric Products, Hicksville, N.Y., paper presented at National SAMPE Technical Conference, October 5-7, 1971, Huntsville, Ala.

(8) Carter, J., and Culp, J. D., "Protective Coatings for Columbium Applied in the Field", Marshall Space Flight Center, Ala., and McDonnell Douglas Astronautics Company-East, St. Louis, Mo., paper presented at National SAMPE Technical Conference. October 5-7. 1971, Huntsville, Ala.

(9) Kaufman, L., and Nesor, H., "Stability Characterization of Refractory Materials Under High Velocity Atmosphere Flight Conditions Part V, Additional Studies", Final Report AFML-TR-69-84, Part V, Manlabs. Inc., Cambridge, Mass., Contract AF 33(615)-3859 (April 1971).

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